NITRATION OF DEXTROSE AND RAFFINOSE

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INTRODUCTION

The investigation which is the subject of this paper had for its object the nitration of dextrose and raffinose, which investigation apparently had not been previously attempted.

E. J. Hoffman and V. P. Hawse [1] have successfully nitrated glucose and obtained crystalline sucrose octa-nitrate.

PREPARATION OF MATERIALS

Treatment of the dextrose.

The dextrose used in the dextrose investigation was Baker Chemical Company C. P. Dextrose. This dextrose contained about 2.5% of moisture, which moisture it was thought best to remove.

The dextrose was dried, using small samples in the following methods -

(1) Heating at 100° for three hours.

(2) Heating at 75° for two hours.

(3) Vacuum dried over sulfuric acid for one week.

(1) J. A. C. S. 41, 235, 1919.

(4) Vacuum dried at 50° c. for five hours.

The dried dextrose from method (1) showed signs of decomposition after one-half hour and decomposition further increased as the drying continued. The final product was decidedly unfit for use, and the method was discarded. The dried dextrose from method (2) showed less decomposition, but it was also unfit for use. By method (3) was obtained a dry dextrose, which was used in the first nitration run on the dextrose, however the mass dried was very small, and the process required a long time.

Method (4) was run as a test of vacuum drying. A 10.9160 gram sample lost 0.1418 grams of moisture, or a 1.289% loss. The vacuum was pulled by a high vacuum pump for the five hours of the test. All of the dextrose was then dried according to method (4), keeping the temperature around 50° C. in the day time, and allowing it to fall to room temperature at night. The vacuum was kept by the vacuum pump during the week of drying. The dried dextrose was transfered to desiccators and kept over concentrated sulfuric acid.

Treatment of the raffinose.

The raffinose used was Kahlbaum C. P. raffinose, a crystalline material, previously dried, and used without further treatment.

Purification of the acetone.

500 grams of sodium bisulfite were dissolved in 700 cc. of water. The resulting solution was cooled below 15° C., placed in two, one-liter, beakers, half in each, and 250 cc. of crude acetone was added slowly to each, keeping the temperature below 15° C., with stirring. The solution was then allowed to stand overnight, out of doors, the beakers being kept covered with watch glasses.

After the precipitation was complete, the compound was scraped out into cheese cloth in a large Beuchner funnel, and sucked as dry as possible. It was not washed. It was then allowed to dry in the air, by spreading out into thin layers, until no odor of methyl alcohol could be detected. The dry bisulfite compound was then weighed, and placed in a two liter distilling flask. For every 100 grams of the bisulfite compound, 30 grams of sodium hydroxide was dissolved in 90 cc. of water and placed in a separatory funnel in the neck of the flask. The distilling flask was then connected to a condenser for distillation from a steam bath. Water was turned into the condenser and the sodium hydroxide added drop by drop through the funnel. When all was added, steam was turned into the bath, and the liquid distilled until no more acetone came over. Calcium oxide was then added to the distillate and it was distilled again. The acetone was then ready for use.

Standard acid and base solutions.

Standard hydrochloric acid solution was made according to the usual laboratory proceedure, using redistilled hydrochloric acid, and standardizing against purified sodium bicarbonate. A two tenths normal acid was prepared.

The standard base was also made by the usual laboratory method, using c. p. sodium hydroxide, and standardizing against the previously prepared two tenths normal acid solution.

EXPERIMENTAL

The method of nitration and purification adopted for preliminary nitration was that of Hoffman and Hawse (1), in their experiment # 4, modified somewhat to fit materials at hand.

Experiment # 1.

100 cc. of freshly prepared nitric acid, prepared by distilling 150 cc. from a mixture of 300 cc. of nitric acid (sp. gr. 1.42) and sulfuric acid, 600 cc., (sp. gr. 1.84), was cooled below - 5°C. and to it added slowly 10 grams of the dried dextrose, stirring the acid continuously during the

(1) Loc. cit.

addition of the sugar. 200 cc. of sulfuric acid, cooled below - 5° C., was then added drop by drop to the mixture over a period of two hours, stirring the mixture continuously during the acid addition and for one-half hour in addition. When stirring was stopped the nitrated product, which separated from the acid mixture, was removed from the cold mixture, placed in ice water, washed thoroughly with six changes of ice water, and lastly washed with iced distilled water. The product remaining was a white pasty mass, stiff when at around zero degrees, and becoming more fluid on warming to room temperature. After washing, the mass was dissolved in ethyl ether and the resulting solution washed with sodium bicarbonate solution. When the solution separating from the ether layer showed basic to litmus the washing with the bicarbonate was discontinued and the ether washed with distilled water until the wash water tested neutral. The ether solution was then allowed to stand overnight to allow further separation of the ether and water. The ether was then evaporated from the solution in a vacuum desiccator, yielding a sticky and pasty mass.

This nitration was run more as a test of the method and the final product was not analyzed.

Experiment # 2.

The nitration in this experiment was carried out as in experiment # 1. The temperature of the mixture during the acid addition and stirring varied between - 7° and - 5° C.

The product was similar to that obtained in experiment 1, and was treated in the same manner. After evaporation of the ether, a residue was obtained which was an amber tinted pasty mass, which became fluid on heating. This residue was dissolved in absolute alcohol, in which it was fairly soluble, and the alcohol slowly evaporated, in an effort to obtain crystals, only a pasty mass similar to that from the ether solution was obtained.

Experiment 3.

This experiment was performed as were the preceding experiments. Carbon dioxide snow was used as the cooling agent, and the initial temperature was below - 20° C. The temperature varied from - 20° to + 5° and then to 0° C. The product obtained was similar to that obtained from the other experiments. The ether solution upon being washed with water yielded an emulsion which settled very slowly, and was allowed to stand over night in a separatory funnel. The water that separated was slightly acid, and the solution was washed again. This washing also formed an emulsion and again an emulsion was formed which was difficult to settle, and had to be left overnight. Upon standing the liquids separated leaving a milky ether layer. On evaporation a product was obtained similar to that from experiments 1 and 2.

Experiment 4.

This experiment was performed as was experiment 1. After the addition of approximately half of the acid and dextrose mixture, a large amount of solid collected on the stirrer. The temperature was kept below - 5° C. during the nitration. The product obtained was similar to that from the other experiments and was treated in the same manner. The final product was also similar to that of the others.

Experiment 5.

The method for this nitration differed slightly from that of the others. 10 grams of dextrose were dissolved in 50 cc. of fuming nitric acid cooled to - 10° C. The resulting solution was kept cooled below zero and added slowly to a mixed acid containing 200 cc. of sulfuric acid and 50 cc. of fuming nitric acid, cooled below zero. The mixture was stirred during the addition of the sugar solution and for an additional half hour after all had been added. The stirring was then stopped and the product removed from the nitrating medium. The nitrated product was washed with ice water and dissolved in anhydrous ether. Upon the addition of the ether, some of the acid mixture held in the nitrate became diluted and warmed and attacked the product. There was a large evolution of nitrogen dioxide fumes and the nitrate was destroyed.

Experiment 6.

The nitration in this experiment was carried out as was

experiment 5. The nitrated product separated during the nitration as a white solid on the stirrer. After the addition of all the acid solution and stirring for one half hour in addition, the product was removed and treated as in the previous experiments. The final product was also similar to the others.

Experiment 7.

This experiment was performed as was experiment 5. The product was also similar to that from the others.

Nitration of raffinose.

Experiment 1.

5 grams of the raffinose were dissolved in 50 cc. of fuming nitric acid cooled below - 10° C. The cold solution was then added, drop by drop, to a mixed acid containing 50 cc. of fuming nitric acid and 200 cc. of concentrated sulfuric acid, cooled below - 10° C. The acid mixture was kept cooled below - 10° C. during the addition of the sugar solution and for an additional half hour, with constant stirring. When stirring was stopped no solid separated that could be removed with the stirrer, so the mixture was poured in a small stream into an ice and water mixture which was kept at zero and stirred. This required about ten liters of ice water. The resulting solution was filtered using suction, and the precipitate washed with ice water. The precipitate

obtained was a fine white powder when dried by suction. It was removed from the filter paper and dissolved in ether. A residue was left which was insoluble in ether, but the amount was very small. The ether solution was washed until clear, and allowed to stand overnight. The water that separated was then drawn off, and the ether evaporated partially. A solid separated which was removed from the solution. It was slightly gummy and seemed to contain several different solids since it was white in spots and streaked with cream. This solid was designated as A. The ether solution was further evaporated until about three cubic centimeters of a very viscous solution remained, and to this solution 15 cc. of absolute alcohol was added and a large amount of fine white solid separated. This solid was then extracted with a small amount of ether, and this ether solution evaporated, yielding a fine white solid when a few cc. of alcohol were added to the final viscous solution. This solid was designated as B.

Solid A was then treated with absolute alcohol, in which very little of the solid seemed to dissolve. The residue left from the alcohol extraction was placed in a vacuum desiccator and the alcohol evaporated, leaving a hard white solid residue which was designated as A1.

The residue from solid B was dissolved in a large excess of ether, and to it was added the absolute alcohol wash from solid A. This solution was then evaporated, leaving a white powder similar to that of B. Designated as C.

Solids A1, B and C were kept in a vacuum desiccator for one week to remove as much of the residual solvent as possible.

Experiment 2R.

This experiment was performed as was experiment 1R, but the filtered solid was treated in a different manner.

The solid was dissolved in ether and the ether evaporated, leaving a white residue. The solid was then treated with absolute alcohol, in which it was partially soluble. The alcohol was evaporated slowly, and during the evaporation a fine white precipitate appeared. When all but a few cc. of the alcohol had evaporated, the precipitate was filtered and washed with fresh alcohol. It was then dissolved in fresh alcohol and the solution again evaporated, leaving a fine white solid, which was filtered and dried in the vacuum desiccator. Solid designated as D.

The residue from the alcohol extraction was treated with ether, part failed to dissolve. The ether solution was then added to the residual and wash alcohol from solid D. The resulting solution was then evaporated leaving a residue which was designated as F. The part that failed to dissolve in the ether was designated as E.

These solids were also kept in the vacuum desiccator.

Nitrogen determinations.

The nitrogen content of the nitrated dextrose and raffinose was determined by the Gunning Method, modified to include nitrate nitrogen.

Approximately 0.50 grams of the nitrate was weighed out and placed in a Kjeldahl digestion flask and to it added 30 cc.

of concentrated sulfuric acid containing 3 grams of salicylic acid, and allowed to stand for ten minutes. 5 grams of sodium thiosulfate were added and the flask heated for 5 minutes. Cooled and 10 grams of potassium sulfate added and the flask heated until the remaining solution was colorless.

The solution was then diluted with 200 cc. of distilled water, 0.5 grams of tin shot added and the flask connected to a condenser for distillation of the ammonia. 50 cc. of a saturated solution of sodium hydroxide were then added down the sides of the flask and the contents mixed by shaking. Distillation was then started and the ammonia distilled into 50 cc. of standard hydrochloric acid. The excess acid was then neutralized with standard base.

In the analysis of the raffinose nitrate it was found necessary to cool the sulfuric acid and salicylic acid mixture to below zero before the addition to the flask. This was done to prevent the oxidation of the nitrate which was very easily ignited. The cold solution was allowed to warm up slowly before the addition of the thiosulfate, and was kept cooled after its addition for about fifteen minutes. After this precaution the analysis was carried on as given, and proceeded smoothly.

Percentage nitrogen.

The dextrose nitrate analyzed 13.65% nitrogen as against 17.28% for the theoretical glucose pentanitrate.

The raffinose nitrate analyzed 15.5% as against 16.0% for the theoretical nitrate.

Viscosity of acetone solution.

Using solid from experiment 2R a 2% solution of the nitrate in purified acetone was made up and the viscosity of the resulting solution was determined at 25° C. The viscosity of the purified acetone was also determined.

The viscosity of the 2% solution was 0.336 centipoises.

The viscosity of the purified acetone was 0.344 centipoises.

DISCUSSION

The method of nitration which gave the best apparent results for the nitration of the dextrose was that used in experiments 5, 6, and 7. From these experiments there was obtained a larger amount of solid product and when cold it was much less viscous than that from the previous experiments.

The method for the nitration of the raffinose yielded a white crystalline nitrate that analyzed near that for the theoretical nitrate in percentage nitrogen.

The temperature was kept low to prevent the oxidation of the primary alcohol group and, in the case of the raffinose, to prevent the hydrolysis of the sugar into the lower sugars, glucose, fructose and galactose.

The analysis of the nitrated products from the nitration of dextrose gave evidence that the mass contained a large amount of the lower nitrates. This might possibly be explained by the separation of the solid during the stirring, which prevented the acid from thoroughly nitrating the dextrose.

The nitrated dextrose was soluble in ether, acetone, and to a much less extent in absolute alcohol. The raffinose nitrate was soluble in ether, acetone and absolute alcohol. This work might be further continued to find more suitable solvents.

By the choice of solvents it might prove an easy process for the separation of the lower nitrates if selective solvents were known. Crystalline dextrose nitrate might easily be prepared by this manner.

The nitrated raffinose proved to be an explosive and further work might give a use for the nitrate along this line.